Morphology control in organic bulk-heterojunction solar cells containing merocyanines

Klaus Meerholz, Nils Michael Kronenberg, Hannah Bürckstümmer, Vera Steinmann, Marcel Gsänger, Manuela Deppisch, Markus Kaiser, and Frank Würthner

Molecular engineering of dyes and deposition-technique optimization enhance performance.

Active-layer morphology control is of paramount importance for the performance of bulk-heterojunction (BHJ) organic solar cells (OSCs). Charge-carrier formation in OSCs takes place only at the interface between the donor and acceptor compounds. Therefore, only photons that are absorbed within the exciton diffusion length from the interface can contribute to the device photocurrent. Electron and hole transport occurs by hopping through the acceptor and donor phases, respectively. Consequently, the morphology of a BHJ solar cell, which is comprised of an interpenetrating bicontinuous network, must assure a large interface between both phases, as well as continuous pathways to both electrodes.

In our research on the application of merocyanine (MC) dyes as donor component in solution-processed BHJ OSCs, we encountered the limit of ‘traditional’ protocols for morphology manipulation in polymeric BHJ solar cells: neither post-production heat treatment nor use of different solvents or solvent additives led to significant improvements in device performance. Therefore, we sought an alternate method of controlling MC solar-cell morphology.

MCs are traditional, low-molecular-weight colorants that are widely applied in textile coloration and for printing purposes. We successfully introduced this material class as donor in solution-processed BHJ solar cells, in combination with the soluble fullerene derivative phenyl-C_{61}-butyric acid methyl ester (PCBM), indicating a higher degree of crystallization for HB194 in both the neat MC sample and the blend. θ: Diffraction angle. (b) Chemical structures of MD376 and HB194. (c) Current-density/voltage (JV) curves. (d) UV-visible spectra of MD376 and HB194 bulk-heterojunction solar cells containing 75 and 55% by weight of PCBM, respectively, indicating enhanced cell efficiency and adaption to solar emission. absorption coefficient (expressed as mole fraction).

Figure 1. (a) Powder x-ray diffractograms (in arbitrary units, a.u.) of the merocyanines (MCs) MD376 and HB194 as neat drop-cast MC films and in blends with the acceptor phenyl-C_{61}-butyric acid methyl ester (PCBM), indicating a higher degree of crystallization for HB194 in both the neat MC sample and the blend. θ: Diffraction angle. (b) Chemical structures of MD376 and HB194. (c) Current-density/voltage (JV) curves. (d) UV-visible spectra of MD376 and HB194 bulk-heterojunction solar cells containing 75 and 55% by weight of PCBM, respectively, indicating enhanced cell efficiency and adaption to solar emission. absorption coefficient (expressed as mole fraction).

Formation of strongly bound centrosymmetric aggregates on the supramolecular level. However, the remaining polarity still results in strong absorption and high permittivity. Both properties are beneficial for OSCs.

Since the periphery of the dye is readily altered by the alkyl substituents attached to the dye core, modification of thermodynamic properties (through influencing dye morphology in the solid state) can be achieved without significantly altering the
Figure 2. (a) Measured open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), fill factor (FF), and power-conversion efficiency (PCE) of HB194 solar cells with active layers (of thickness $d_{total}$) deposited by spin coating from solution (blue, acceptor: PCBM) and thermal evaporation from vacuum (red, acceptor: C$_{60}$). (b) Scanning-transmission electron microscopy images of active layers, indicating the smaller scale of phase separation in layers deposited from vacuum. SOL: Spin-coated in solution. VAC: Thermal evaporated in vacuum.

energy levels of the compounds. We found that replacing the linear alkyl chain of MD376 with a cyclic alkyl group in HB194—see Figure 1(b)—leads an increase in dye rigidity on the molecular level and, therefore, to an enhanced degree of dye crystallinity on the supramolecular level: see Figure 1(a). Because of the higher crystallinity, solar cells containing HB194 feature more efficient phase formation. Thus, hole-transport properties through the MC phase in the blend improved, while the optimum donor-to-acceptor ratio in the bulk was shifted in favor of the MC. In addition, the cell-absorption profile was more adapted to solar emission: see Figure 1(d). Both effects result in increased device photocurrent. Accordingly, tailoring the MC’s alkyl periphery results in changes comparable to the effect of heat treatment in some polymeric solar cells. Cell efficiency increased from 1.5 to 2.6%: see Figure 1(c).

We achieved a further performance gain for HB194 by changing the processing technique. In OSC preparation, one generally distinguishes between wet chemical techniques, such as spin coating, and thermal deposition from high vacuum. Both techniques require specific physical material properties. Since MCs such as HB194 feature both high solubility and thermal stability, they can be deposited using either method. Thus, only one modification must be made to the acceptor using the soluble fullerene derivative PCBM for spin coating and C$_{60}$ for evaporation.

While adjusting deposition technique did not significantly alter the optimum active-layer thickness—see Figure 2(a)—we found large differences in the parameters of the two cells. HB194 solar cells with solution-processed active layers exhibited an approximately 200meV higher open-circuit voltage ($V_{OC}$)—see Figure 2(a)—while the short-circuit current density ($J_{SC}$) clearly increased for cells with vacuum-deposited active layers (11 versus 7mA/cm$^2$): see Figure 2(a). We measured remarkable power-conversion efficiencies of up to 4.9% for thermal-evaporated devices. We attribute the difference in $V_{OC}$ to changes in the highest-occupied molecular-orbital energy of the MC, induced by the degree of aggregation, which is itself a function of deposition rate. Additionally, the lowest-unoccupied molecular-orbital levels of the acceptor vary in both device types.

The absorption of both cells was roughly identical, while the vacuum-deposited device exhibited significantly higher $J_{SC}$ values: see Figure 2(a). An investigation of the morphology using scanning-transmission-electron microscopy demonstrated that phase separation occurs on a smaller scale in layers deposited from vacuum: see Figure 2(b). Thus, exciton separation can take place more effectively, resulting in higher $J_{SC}$ values. Measurements of donor-photoluminescence quenching also support our finding of a more intimate mixture in vacuum-deposited blends.

In conclusion, we have demonstrated two methods capable of influencing the morphology and, thus, the performance of BHJ solar cells containing MC dyes. In these devices, protocols traditionally applied for morphology control in polymeric devices failed, while successful results were achieved through tailoring dye crystallinity and deposition technique. Our successful evaporation of MCs paves the way for MC tandem solar cells. In this context, the broad tunability of MC-dye absorption properties and the application of near-IR absorbing MC in OSCs is particularly promising. Thus, we expect MC tandem solar cells to harvest a great proportion of solar emission.

Author Information

Klaus Meerholz, Nils Michael Kronenberg, Vera Steinmann, and Markus Kaiser
Department of Chemistry
University of Cologne
Cologne, Germany

Hannah Bürckstümmer, Marcel Gsänger, Manuela Deppisch, and Frank Würthner
Institute of Organic Chemistry
University of Würzburg
Würzburg, Germany

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